KINETIC MODELING OF GAS-PHASE AROMATICS OXIDATION AND GROWTH

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INTRODUCTION

The kinetics of aromatics oxidation and growth are studied using ab initio quantum chemistry methods, RRKM calculations, and detailed kinetic modeling. This work is motivated by both fundamental and practical considerations. While significant advance has been made in the understanding of the oxidation kinetics for aliphatic hydrocarbon combustion, comparatively fewer studies have been conducted on aromatics.[1,2] Such a disparity in emphasis is expected because of the significantly more complex nature of the aromatic kinetics. It is also obvious that since most practical fuel blends consist of large amounts of aromatics, satisfactory modeling and manipulation of the combustion processes would not be possible without a quantitative description of their oxidation kinetics. Such a concern is further substantiated by recognizing the role of aromatics kinetics in engine knock,[3] in soot production,[4-12] in the emission of polycyclic aromatic carcinogens,[13] in fullerene synthesis,[14] and in fuel-cell technology.[15,16]

Previously, a detailed kinetic model of benzene and toluene oxidation has been proposed by Emdee, Brezinsky, and Glassman,[2] on the basis of flow-reactor experiments at the temperatures between 1100 to 1200 K and at atmospheric pressure. Benzene oxidation at high temperatures was further examined through detailed kinetic modeling. Several kinetic models have been proposed and tested against experimental data, including the species profiles in the burner-stabilized low-pressure benzene flame[17–19] of Bittner and Howard,[20] and the laminar flame speeds of benzene-air and toluene-air mixtures.[19,21,22] It was shown that the proposed models predicted reasonably well each individual set of the experimental data, but a comprehensive and physically justifiable model, which is capable of closely predicting *all* the available experimental data, is still lacking.

The aim of this work is to develop a comprehensive kinetic model of aromatics oxidation and mass growth in combustion. In this article, we report a preliminary kinetic model, which describes the high-temperature oxidation of benzene and toluene. Numerical results are present and compared to experimental data from previous flow reactor,[2] flame[20,21] and shock-tube studies.[23]

METHODOLOGIES

Quantum Chemical Calculations

We employed Pople's G2 method[24] and its simplified versions[25-29] for the calculations of the thermochemical data, including enthalpy of formation, entropy and heat capacity for the relevant molecular and radical species, and the potential energy surface of chemical reactions. Isodesmic reactions[30] are used to determine the enthalpy of formation. The transition-state structures are initially optimized with the spin-unrestricted Hartree-Fock (UHF) method, employing the split-valence 3-21G basis set. The structures were further optimized at the HF/6-31G(*d*) level and refined at the UMP2(full)/6-31G(d) level. In all calculations, we employed the analytical gradient procedure and the combined Synchronous Transit and Quasi-Newton (STQN) method.[31] The vibrational frequencies were obtained from the geometries optimized at the UMP2(full)/6-31G(d) level of theory.

Rate Coefficient Calculations

Many elementary reactions of aromatics are chemically activated, involving the stabilization and isomerization of the hot adduct. The rate coefficients of these reactions are not known and are determined in the present study using the RRKM method.[32,33] The RRKM parameters, including the vibrational frequencies and rotational constants of the reactants and transition states, are obtained from the quantum chemical calculations. Details of the RRKM computer code are documented elsewhere.[34]

Detailed Kinetic Modeling

A detailed kinetic model of benzene and toluene oxidation at high-temperature is compiled. The model consists of 65 species and 340 elementary reactions. The reaction kinetics of C_1 and C_2 species are based on the GRI-Mech (version 1.2).[35] For large species, the reaction pathways and rate coefficients are obtained from literature data (e.g., ref 36). Many rate parameters are analyzed using the RRKM methods in our previous studies,[37,38] as well as in the present work.

Calculations of the laminar flames are carried out using the Sandia Chemkin-II[39] and Premix[40] codes. The reverse rate coefficients are computed via equilibrium constants. While the thermochemical data of cyclopentadiene and cyclopentadiene

derivatives are obtained through quantum chemical calculations, others are taken from ref 35, and from the compilation of Burcat and McBride.[41] .

RESULTS

The first step during the oxidation of the aromatics is the disintegration of the aromatic ring structure. This is followed by the oxidation of the resulting products to CO and finally to CO_2. Previous studies[2,21] show that the initial oxidation of benzene leads primarily to phenol and phenoxyl, followed by the formation of cyclopentadiene and the cyclopentadienyl radical. The disintegration of the cyclic structure occurs at the stage when the C_5 species are oxidized. It was found that the oxidation of the C_5 species is often the bottle neck during benzene oxidation. Here, we examined the reaction pathway and analyzed reaction rate coefficient for one of these bottleneck reactions, i.e., the thermal decomposition of cyclopentadienone

$$c\text{-}C_5H_4O \rightarrow \text{products} .$$

Figure 1 presents the energy diagram of the above reaction. The rate coefficients computed using the RRKM are shown in the inset. It is seen that unlike the previously proposed pathway, the minimum energy path leads to cyclobutadiene, which may subsequently isomerize to vinylacetylene, or it may dissociate to acetylene.

Figure 2 presents the comparison of the experimental[2] and computed concentration profiles of selected species during benzene oxidation in a flow reactor at 1100 K and with the equivalence ratio equal to 0.67. It is seen that the present kinetic model predicts very well the concentrations of benzene, CO, acetylene, and cyclopentadiene. The model tends to underpredict the concentration of phenol. Figure 3 presents the comparison of species profiles during toluene oxidation at 1190 K and with the equivalence ratio equal to 1.33. Again, the major species profiles, including toluene, CO, benzene, phenol, benzaldehyde, methane, and acetylene are predicted well.

Figure 4 shows the comparison of the experimental[21] and computed laminar flame speeds of benzene- and toluene-air mixtures at atmospheric pressure. It is seen that the kinetic model predicts slightly larger flame speeds than the experimental data for benzene. However, the variation of the flame speed on the equivalence ratio is nicely predicted.

The experimental and computed major and minor species profiles are presented in Figure 5 for a burner-stabilized benzene-oxygen-argon flame at 20 torr.[20] It is seen that the model predicts very well the variation of the major species profile as a function of distance from the burner. The model also predicts well the shape and magnitude of such minor species as the H atom and the OH radical.

In Figure 6, we plot the experimental[23] and computed ignition delay time of a benzene-oxygen-argon mixture at a pressure of 2.5 atm. The present kinetic model appears to overpredict the data slightly, but the variation of the ignition delay on temperature is well reproduced.

DISCUSSION

We have shown that a detailed kinetic model of benzene oxidation can account for the main features of benzene and toluene oxidation under a variety of combustion conditions. Recognizing, however, that many practical combustion devices operate at elevated pressures, it is essential to extend the predictive capability of the model to high pressures as well. Because of the variation of the reaction pathways and rate coefficients as a function of pressure, low-pressure models usually fail when they are used for prediction at high pressures. The inherent reason is that many reactions involving the aromatic species are chemically activated, involving the competition of collisional stabilization and dissociation/isomerization of the hot adduct. For example, the reaction between the cyclopentadienyl and the OH radical initially leads to a vibrationally excited cyclopentadienol, which may be stabilized by collision with other molecules, or it may dissociate to the singlet cyclopentadienylidene + H_2O or c-C_5H_4OH + H. Unlike the reaction pathways at low pressures, the stabilization process becomes favorable at elevated pressures. The change in the reaction product often means a change in the overall fuel destruction routes.

While it is often difficult to obtain reliable fundamental combustion data at elevated pressures, reliable extrapolation of the reaction rate coefficients is now possible with the recent advances in quantum mechanical methods and reaction rate theories. These methods can be and should be used for the further refinement and extrapolation of the base model developed in the present study.

CONCLUSION

A detailed kinetic model of benzene and toluene oxidation is developed. It is shown that the kinetic model predicts reasonably well the available experimental data of benzene and toluene oxidation in flow reactors, flames, and shock tubes.

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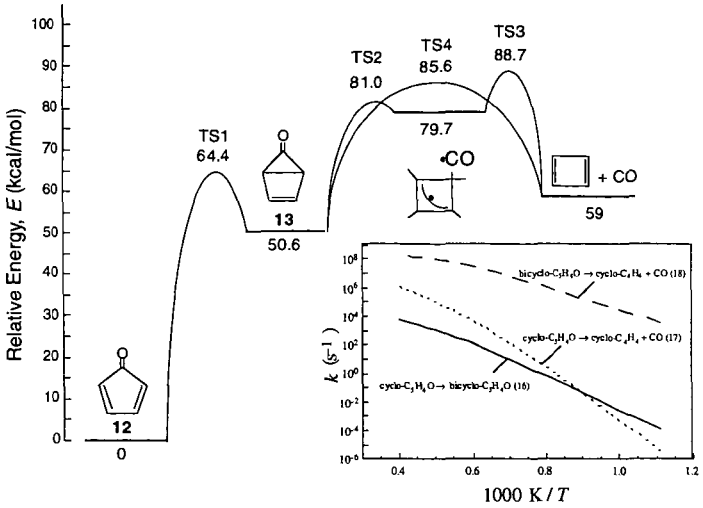

Figure 1. Energy diagram and the rate coefficients (p = 1 atm) computed for the thermal decomposition of cyclopentadienone.

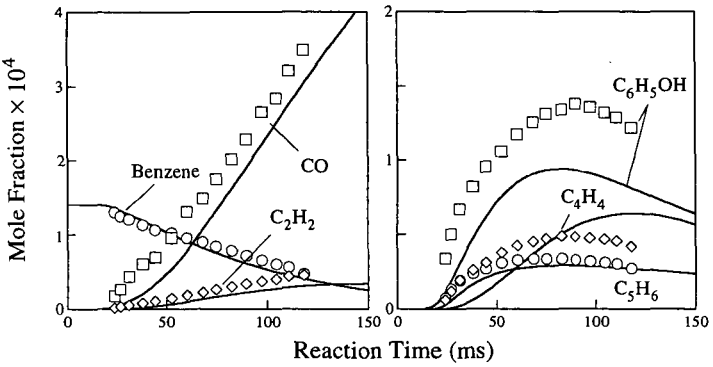

Figure 2. Experimental[2] and computed species profiles for benzene oxidation (0.14% C_6H_6-1.62% O_2-N_2, the equivalence ratio $\phi = 0.67$) in a flow reactor at 1100 K and 1 atm pressure.

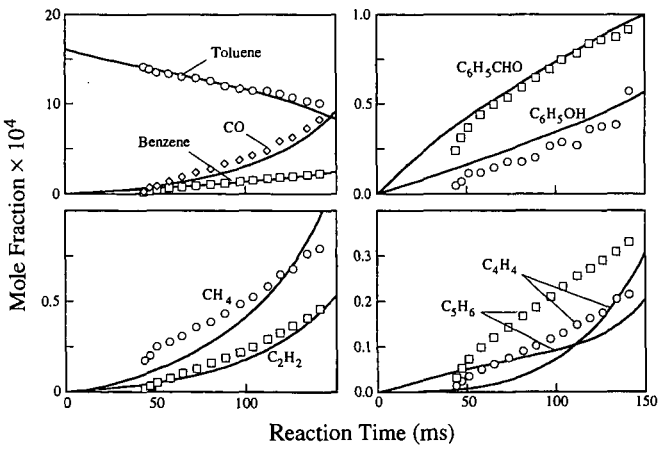

Figure 3. Experimental[2] and computed species profiles for toluene oxidation (0.162% C_7H_8-1.094% O_2-N_2, the equivalence ratio $\phi = 1.33$) in a flow reactor at 1190 K and 1 atm pressure.

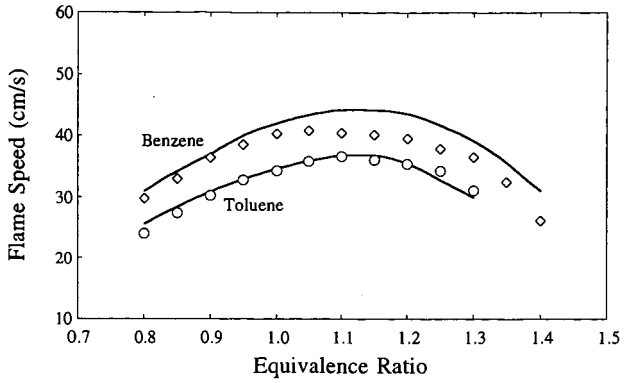

Figure 4. Experimental[21] and computed laminar flame speed of benzene- and toluene-air mixture at 1 atm pressure.

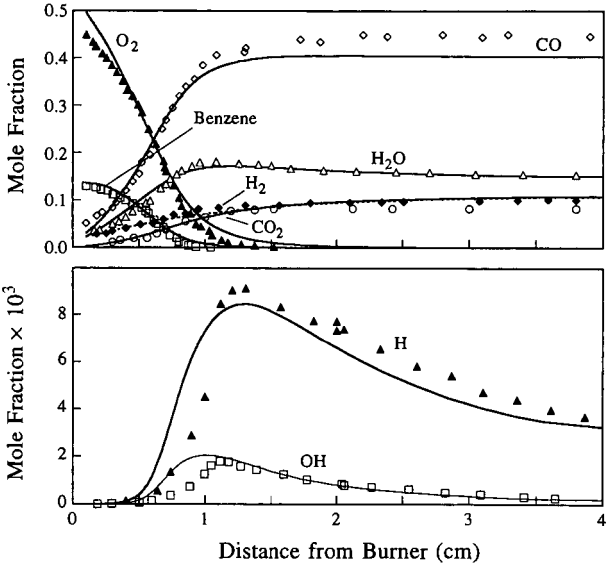

Figure 5. Experimental[20] and computed species profiles in a burner-stabilized laminar premixed flame, burning a 13.5% benzene-56.5 % O_2-Ar mixture at 20-torr pressure.

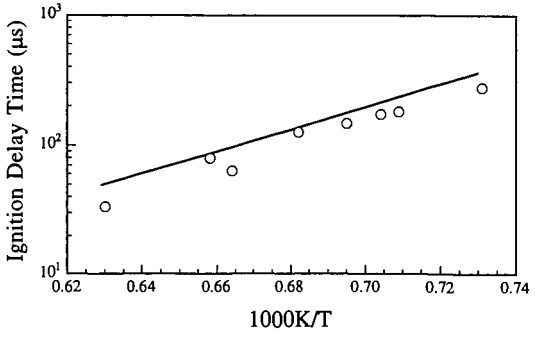

Figure 6. Experimental[23] and computed ignition delay time for a 1.69% benzene-12.675% O_2-Ar mixture at p_5 = ~2.5 atm.